

# THE EFFECT OF $H_2$ PARTIAL PRESSURE AND TEMPERATURE ON CATALYTIC HYDROGENATION WITH $MoS_2$ CATALYSTS

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## INTRODUCTION

Molybdenum-based catalysts have been used extensively for catalytic hydrogenation[1-3]. The type of catalyst, either supported or unsupported, and the preparation and activation procedures can impact catalytic behavior for hydrogenation and coal conversion reactions. This study compared the catalytic hydrogenation and coal conversion observed with preactivated forms of supported and unsupported catalysts. The objective was to utilize model compounds to compare the catalytic hydrogenation activity of these two types of catalysts. The effect of catalyst type, supported or unsupported, on catalytic hydrogenation with and without coal present was studied over a range of pressures, 1.4 MPa (200 psig) - 11.0 MPa (1600 psig)  $H_2$ . The results indicated that catalytic hydrogenation activity was observed at  $H_2$  partial pressures as low as 4.8 MPa (700 psig) with both catalyst types.

## EXPERIMENTAL

**Materials.** ACS grade 1-methylnaphthalene from Fisher Scientific Company, found to be 99% pure by gas chromatography, was used without further purification. Blind Canyon coal, (DECS-6) from the U.S. Department of Energy's Coal Sample Program, was used in these studies. The Blind Canyon coal was a low pyrite bituminous coal with 6.3% ash and 3.7% moisture. A unique, high surface area, molybdenum catalyst was prepared at the U.S. Department of Energy's Pittsburgh Energy Technology Center (PETC). The catalyst consisted of the recovered solid from a semi-batch 1-L stirred autoclave reaction of ammonium heptamolybdate, hydrogen sulfide, and Panasol (a mixture of alkylated naphthalenes) under 17.2 MPa (2500 psi) hydrogen at 700 °K [2-4]. The catalyst contained 50% C, 30% Mo, and 20% S by weight, and possessed a BET surface area of approximately 260 m<sup>2</sup>/g. Supported molybdenum/nickel catalysts, AKZO AO-60 obtained from HTI, Inc. and Shell-324, were also used. Other catalysts tested included two prepared by impregnating carbon black with Mo or Fe (Mo-C-1 and Fe-C-1, respectively), sulfated  $Fe_2O_3$ [5], and carbon black (BET surface area of 490 m<sup>2</sup>/g) obtained from Columbian Chemicals Co.

**Reactions.** Reactions were conducted in a stainless steel batch microautoclave reactor system constructed at PETC. The cylindrical reactor portion has a volume of 43 mL, and the total internal volume, including all tubing and connections, is 60 mL. The reactor was mounted on a rocker arm, which extends into an electrically heated sand bath. In typical experiments, the reactor was charged with various combinations of solvent, coal, catalyst, a sulfur source, and then was pressurized with hydrogen. Unless otherwise stated, a full charge consisted of 6.6 g solvent, 3.3 g coal, 0.1 g catalyst, 0.1 g elemental sulfur, and 6.9 MPa (1000 psi) ambient temperature hydrogen gas. The reactor was then attached to the rocker arm (180 cycles / minute) and plunged into a preheated sand bath, where it was heated up to 700 °K in 2 to 4 minutes. It was held at temperature in the sand bath for 30 minutes, removed and allowed to air cool, typically in less than 5 minutes, to room temperature. The reactor was vented and the gas collected for analysis.

**Sample Work up Procedure and Coal Conversion Calculation.** During work up, the reactor (including tubing) was cleaned and rinsed with tetrahydrofuran (THF). The material collected was combined and filtered through a 0.45 micron filter under nitrogen gas pressure, yielding the "THF solubles" and "THF insolubles." Coal conversion was calculated based on the mass of MAF coal from the measured mass of THF insolubles adjusted for catalyst and coal mineral matter[6].

**Gas and Pressure Analyses.** At the completion of each run, product gases were collected and analyzed at PETC by a previously published method [7]. The product gaseous mixture composed mainly of  $H_2$ ,  $C_1-C_4$ ,  $CO_2$ , and  $H_2S$ , was corrected for non-ideal behavior using an equation of state, and the amount of  $H_2$  consumed was then calculated.

**Solvent Hydrogenation Analysis.** Low-Voltage, High-Resolution Mass Spectrometry (LVHRMS) data were used to calculate solvent hydrogenation. LVHRMS data were obtained on a Kratos MS-50 high-resolution mass spectrometer interfaced to a personal-computer-based data system developed at PETC. Further details on the LVHRMS technique and data reduction routines are provided in references 8 and 9.

## RESULTS AND DISCUSSION

The catalytic hydrogenation of 1-methylnaphthalene using various catalysts was investigated in microautoclave reactors. The results from the catalytic hydrogenation experiments are compared in Table 1. The results in Table 1 seem to indicate that supporting the catalyst (either Fe or Mo) is beneficial for solvent hydrogenation. This is somewhat surprising for the Mo system since as shown in Table 2, the dispersion (physical) for the  $\text{MoS}_2$  catalyst is about the same or slightly greater for the unsupported than the supported catalyst. Also shown in Table 1 is the synergistic effect of having both the sulfated  $\text{Fe}_2\text{O}_3$  and carbon black present during solvent hydrogenation. The  $\text{H}_2$  consumption is much higher with both the sulfated  $\text{Fe}_2\text{O}_3$  and carbon black present than with either used alone and is twice the sum of the  $\text{H}_2$  consumed for the sulfated  $\text{Fe}_2\text{O}_3$  and carbon black each employed separately. In addition, hydrogen consumption using the mixed pair of sulfated  $\text{Fe}_2\text{O}_3$  and carbon black was equal to that of the highly dispersed  $\text{MoS}_2$ . A possible explanation is that the sulfated  $\text{Fe}_2\text{O}_3$  may associate with the carbon black allowing absorbed hydrogen to migrate to the carbon surface (i.e., spillover[10]). This hydrogen could be active and could increase the amount of solvent hydrogenated and the  $\text{H}_2$  consumption. A second possibility is that the presence of the carbon black resulted in a more dispersed form of pyrrhotite. Experiments are being conducted in order to test these possibilities.

**TABLE 1. Effect of Catalyst Type on Solvent Hydrogenation,  
6.9 MPa (1000 psig)  $\text{H}_2$  cold / No coal)**

Catalyst <sup>a</sup>	$\text{H}_2$ Consumed (mMol)	Solvent Hydrogenation (%)
$\text{MoS}_2$ (unsup.)	28	28
Mo-C-1	55	48
AO-60	54	53
Shell-324	52	53
Fe-C-1	38	19
Sulfated $\text{Fe}_2\text{O}_3$	10	na
Sulfated $\text{Fe}_2\text{O}_3$ + Carbon Black <sup>b</sup>	28	na
Carbon Black <sup>b</sup>	4	1
None	5	1

<sup>a</sup>3000 ppm active metal loading used with respect to solvent weight.

<sup>b</sup>1.0 g of Carbon Black added.

**TABLE 2. Catalyst Dispersion**

Catalyst	XRD size (002 plane of Mo, Å)	BET Surface Area ( $\text{m}^2/\text{g}$ )
$\text{MoS}_2$ (unsup.)	<25	260
AO-60	30	162
Mo-C-1	47	na

**TABLE 3. Effect of Catalyst Type on Coal Liquefaction Experiments**

Catalyst <sup>a</sup>	Coal Conversion (%maf coal)	$\text{H}_2$ Consumed (mMol)	Solvent Hydrogenation (%)
$\text{MoS}_2$ (unsup.)	95	55	13
AO-60	87	32	10
Shell-324	81	39	9

<sup>a</sup>1000 ppm active metal loading used with respect to maf coal weight.

In the presence of a complex system, such as coal, the trends are altered, as shown in Table 3. There does not appear to be a significant difference between the supported and unsupported catalysts. If anything, the unsupported catalysts appear to outperform the supported catalysts. This is not surprising in that the effect of the addition of coal on the suppression of catalytic

hydrogenation activity of both the unsupported and supported catalysts has been previously reported [11,12]. The unsupported MoS<sub>2</sub> and supported AO-60 catalysts are compared with respect to the effect of H<sub>2</sub> pressure on H<sub>2</sub> consumption and coal conversion in Figures 1 and 2 respectively. Figure 1 shows that the H<sub>2</sub> consumption for the MoS<sub>2</sub> with no coal present was lower than that of the supported catalyst at all the pressures tested. However, as shown in Figures 1 and 2, the H<sub>2</sub> consumptions and coal conversions, with coal present, are similar for both catalysts.

## SUMMARY

The focus of this study was to compare the catalytic hydrogenation observed with supported and unsupported catalysts. In the tests with the 2-ring aromatic solvent (1-methylnaphthalene), the supported catalysts showed superior catalytic hydrogenation performance. Even the case where the support and catalyst precursor were added separately (Sulfated Fe<sub>2</sub>O<sub>3</sub> + Carbon Black), the hydrogen consumption was greater than the unsupported catalyst alone. However, the performance of supported and unsupported catalysts in hydrogenation and conversion were comparable when coal was added to the system. Also, at an initial H<sub>2</sub> pressure of 6.9 MPa (1000 psig) cold with coal present, the H<sub>2</sub> consumptions and coal conversions are slightly higher for the unsupported catalyst experiments.

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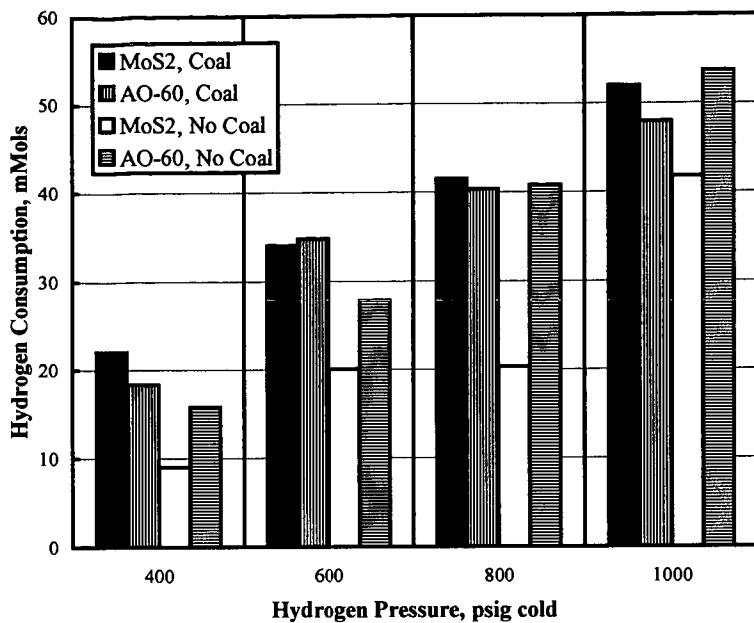


Figure 1. Effect of Pressure on Hydrogen Consumption

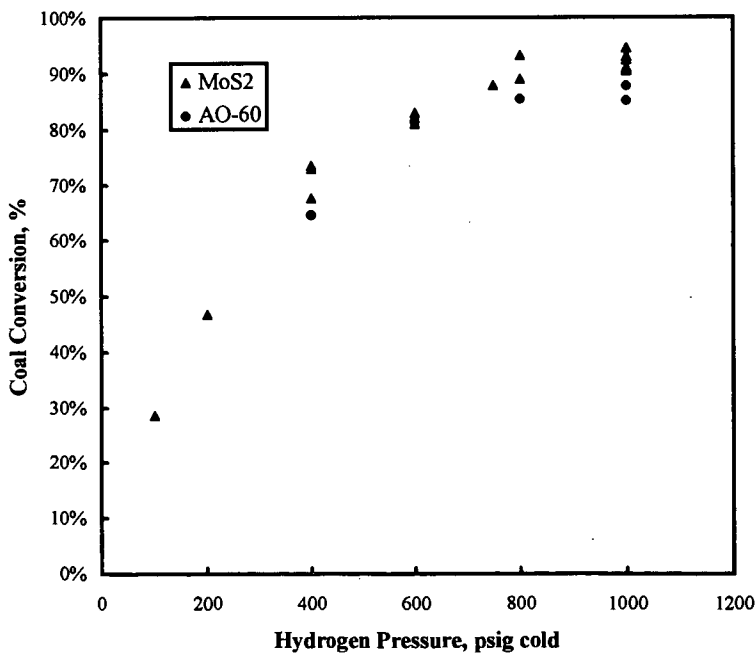


Figure 2. Effect of Pressure on Coal Conversions